Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1364). Services for accessing these data are described at the back of the journal.

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(15-Crown-5)caesium Dicopper(I) Triiodide, (15-Crown-5)potassium Dicopper(I) Triiodide and (15-Crown-5)rubidium Dicopper(I) Triiodide

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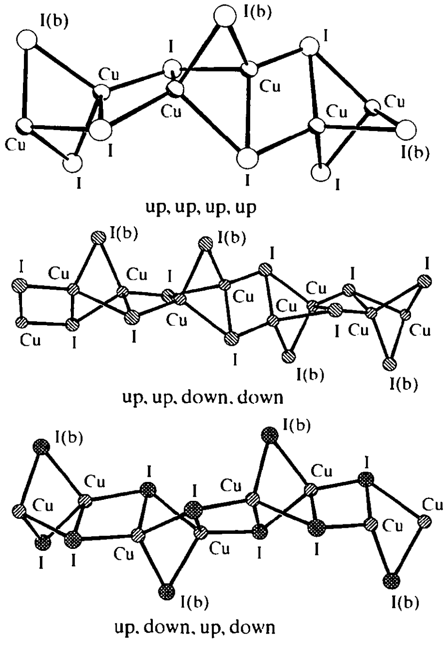
Abstract

(15-Crown-5)caesium triiododicopper(I), [Cs($C_{10}H_{20}O_5$)][Cu_2I_3], (15-crown-5)potassium triiododicopper(I), [K($C_{10}H_{20}O_5$)][Cu_2I_3], and (15-crown-5)rubidium triiododicopper(I), [Rb($C_{10}H_{20}O_5$)][Cu_2I_3], are isostructural. They contain a polymeric $Cu_2I_3^-$ moiety, *catena*-poly[[copper(I)-μ_2-iodo-copper(I)]-di-μ_3-iodo], which may be viewed as a series of opposite edge-sharing Cu_2I_2 rhombs, with alternate units bridged by an additional I atom in an up, up, down, down pattern.

Comment

Copper(I) halide complexes have been observed to exhibit a wide variety of stoichiometries depending upon the identities of halide, counterion, solvent and conditions of synthesis (Rath & Holt, 1986). These complexes may be viewed as composed of rhombs of alternating Cu and halide atoms which may be combined in various ways. While many of these are discrete cluster species (Hu & Holt, 1994*a*,*b*), others such as $Cu_3I_4^-$ (Rath & Holt, 1985) and $Cu_2I_3^-$ are polymeric in nature.

The $Cu_2I_3^-$ polymer may be viewed as a chain of Cu_2I_2 rhombs which share opposite edges, with an additional I atom bridging the Cu atoms of every alternate rhomb. However, the bridging I atoms may show bridging on the same side of the polymeric sheet, bridging in the sequence two up, two down, *etc*., or bridging on alternating sides of the polymer (Fig. 1).



up, up, up, up

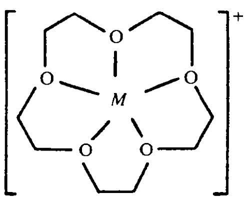
up, up, down, down

up, down, up, down

Fig. 1. Three variations of bridging.

Only one example is known in which all bridging is on the same side of the polymeric sheet: [2,4,6-triphenylthiopyrylium][Cu_2I_3] (Batsanov *et al.*, 1982) crystallizes with a helix-like tertiary structure in which the bridging I atoms project outwards (up, up, up, up; Fig. 1).

A further group of $Cu_2I_3^-$ species is seen to display a pattern of up, up, down, down bridging species. [Cs(15-crown-5)][Cu_2I_3], (I), and [Rb(15-crown-5)]-[Cu_2I_3], (III), are previously unreported and display an up, up, down, down pattern.



(I) M = Cs
(II) M = Rb
(III) M = K

[K(15-crown-5)][Cu_2I_3], (II), was originally reported to have a triclinic cell (Rath & Holt, 1985). We find that the original space group was incorrect and should have been $C2/c$. Since symmetry elements within the cluster often display a significant influence on the wavelength of maximum emission of copper(I) halide species, we have redetermined the structure in the correct space group.

$Cu_2I_3^-$ polymers with alternating up, down, up, down projections of bridging iodides are discussed in the following paper (Nurtaeva *et al.*, 1998).

The title structures show close Cu···Cu contacts across bridged rhombs and greater Cu···Cu separations in the non-bridged rhombs. Cu···Cu separations across bridged rhombs range from 2.430 (9) to 2.480 (7) Å, and those across non-bridged rhombs range from 2.579 (10) to 2.697 (6) Å; the corresponding Cu···Cu separations in [2,4,6-triphenylthiopyrylium][Cu_2I_3] are 2.479 and 2.634 Å, respectively.

The Cu—I distances involving the μ_2-bridging I atoms are in the range 2.590 (6)–2.650 (4) Å in the three title structures, similar to those of 2.642–2.651 Å reported for the all-up variant.

All known Cu_2I_3 polymers display alternation of long and short Cu—I distances along the edges of the polymeric sheet, with the shorter distances forming the edges of unbridged rhombohedra. Sequential Cu—I distances of 2.491 (7) and 2.882 (6) Å were found along one edge of the polymeric sheet of (I), and sequential Cu—I distances of 2.751 (6) and 2.502 (7) Å were found along the opposite edge; for (II), these distances are 2.492 (5) and 2.714 (4) Å, and 2.887 (4) and 2.508 (5) Å; for (III), the alternation is 2.538 (5) and 2.917 (4) Å, and 2.747 (4) and 2.529 (6) Å. Batsanov *et al.* (1982) reported similar long–short sequences of 2.522 and 2.779 Å, and 2.541 and 2.847 Å. Thus details of bonding are similar and appear to be independent of the tertiary structure of the polymer.

The Cu_2I_3 polymers crystallize with inversion centers located in the middles of unbridged rhombs between up and down bridged units and with twofold axes passing through the centers of unbridged rhombs joining up, up or down, down bridged units.

The cations are found between the adjacent projecting I atoms and display three ionic interactions with I atoms of the same chain [averages: K···I 3.624 (4), Rb···I 3.726 (3) and Cs···I 3.809 (6) Å]. These interactions undoubtedly influence the up, up, down, down orientation of bridging I atoms (Fig. 2).

Most unexpectedly, none of the three title structures emits in the visible region when excited with ultraviolet radiation. Other polymeric copper(I) halide species have been found to display solid-state emission and thus further work is aimed at examination of the molecular orbital distributions of the Cu_2I_3 polymer.

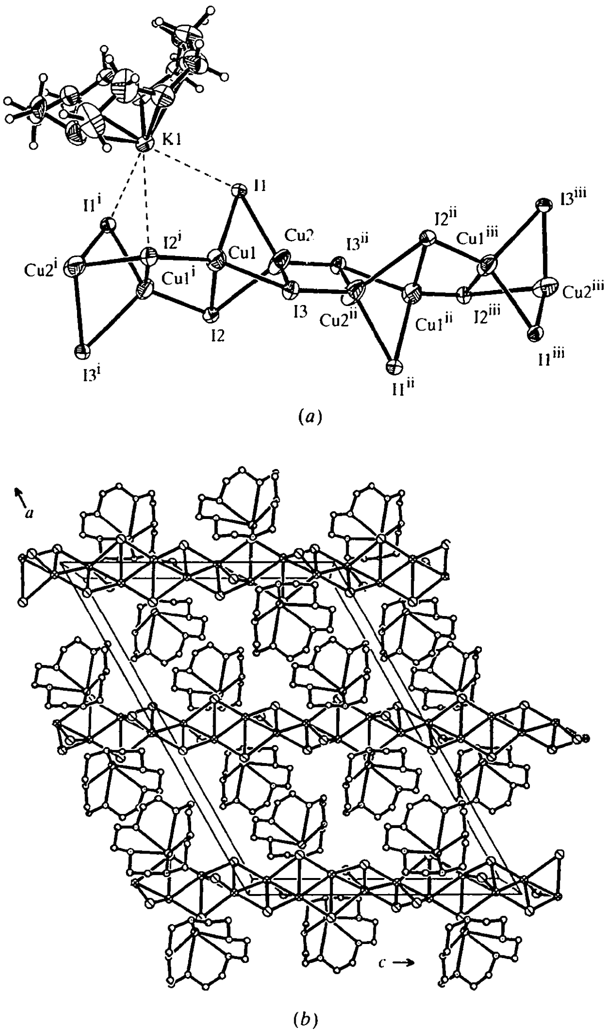


Fig. 2. (*a*) (15-Crown-5)potassium dicopper triiodide, (II) [symmetry codes: (i) $1-x, y, \frac{1}{2}-z$; (ii) $1-x, -y, -z$; (iii) $x, -y, -\frac{1}{2}+z$], with ellipsoids shown at 50% probability. (*b*) Projection of (II) down the *b* axis.

Experimental

To prepare compound (I), CuI (0.382 g, 2 mmol), 15-crown-5 (0.440 g, 2 mmol) and CsI (0.780 g, 3 mmol), dissolved in 3 ml water, were mixed with 15 ml acetone and 1 mmol ascorbic acid [to prevent copper(I) oxidation]. The mixture was heated under reflux for 22 h. The resulting hot yellow solution was filtered and upon standing for 2 d, large colorless polyhedra formed. To prepare compound (II), CuI (0.382 g, 2 mmol), KI (0.498 g, 3 mmol), dissolved in 3 ml water, and 15-crown-5 (0.440 g, 2 mmol) were mixed with 15 ml of acetone and 1 mmol of ascorbic acid [to prevent copper(I) oxidation]. The mixture was heated under reflux for 8 h. The resulting yellow solution was filtered immediately and upon standing for 2 d, large colorless polyhedra crystallized. To prepare compound (III), a mixture of CuI (0.382 g, 2 mmol), 15-crown-5 (0.440 g, 2 mmol) and RbI (0.636 g, 3 mmol), dissolved in 3 ml water, was heated under reflux in 15 ml acetone in the presence of ascorbic acid [to prevent copper(I) oxidation]. After 24 h heating, the resulting yellow solution was filtered and allowed to stand for one month, whereupon yellow plates and colorless rod-like crystals appeared.

Compound (I)

Crystal data

$[Cs(C_{10}H_{20}O_5)][Cu_2I_3]$
$M_r = 861.0$
Monoclinic
$C2/c$
$a = 25.19\ (3)$ Å
$b = 11.177\ (12)$ Å
$c = 16.86\ (3)$ Å
$\beta = 120.36\ (7)°$
$V = 4096\ (10)$ Å^3
$Z = 8$
$D_x = 2.798$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2.855$–$11.491°$
$\mu = 8.38$ mm^{-1}
$T = 301$ K
Rhombohedron
0.20 × 0.15 × 0.10 mm
Colorless

Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Sheldrick, 1990)
$T_{\min} = 0.108$, $T_{\max} = 0.433$
6938 measured reflections
5956 independent reflections
1978 reflections with $F > 6\sigma(F)$

$R_{\rm int} = 0.060$
$\theta_{\max} = 30.0°$
$h = -1 \rightarrow 35$
$k = -1 \rightarrow 15$
$l = -23 \rightarrow 20$
3 standard reflections every 97 reflections intensity decay: negligible

Refinement

Refinement on F
$R = 0.060$
$wR = 0.069$
$S = 1.36$
5956 reflections
191 parameters
H atoms constrained
$w = 1/[\sigma^2(F) + 0.0008F^2]$

$(\Delta/\sigma)_{\max} = 0.068$
$\Delta\rho_{\max} = 0.95$ e Å^{-3}
$\Delta\rho_{\min} = -1.19$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond distances (Å) for (I)*

I(1)—Cu(1)	2.607 (6)	I(3)—Cu(2^{ii})	2.502 (7)
I(1)—Cu(2)	2.590 (6)	Cu(1)···Cu(2)	2.430 (9)
I(2)—Cu(1)	2.843 (6)	Cu(1)···Cu(1^{i})	2.690 (8)
I(2)—Cu(2)	2.882 (6)	Cu(2)···Cu(2^{ii})	2.579 (10)
I(2)—Cu(1^{i})	2.491 (7)	Cs(1)···I(1^{i})	3.838 (6)
I(3)—Cu(1)	2.751 (6)	Cs(1)···I(2^{i})	3.834 (6)
I(3)—Cu(2)	2.750 (6)	Cs(1)···I(1)	3.755 (6)

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$.

Compound (II)

Crystal data

$[K(C_{10}H_{20}O_5)][Cu_2I_3]$
$M_r = 767.1$
Monoclinic
$C2/c$
$a = 23.818\ (14)$ Å
$b = 10.956\ (6)$ Å
$c = 17.071\ (10)$ Å
$\beta = 119.75\ (2)°$
$V = 3868\ (4)$ Å^3
$Z = 8$
$D_x = 2.631$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 43 reflections
$\theta = 5.242$–$12.427°$
$\mu = 7.206$ mm^{-1}
$T = 298$ K
Polyhedron
0.20 × 0.15 × 0.10 mm
Colorless

Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Sheldrick, 1990)
$T_{\min} = 0.243$, $T_{\max} = 0.486$
6605 measured reflections
5650 independent reflections
2175 reflections with $F > 5.5\sigma(F)$

$R_{\rm int} = 0.081$
$\theta_{\max} = 30.0°$
$h = -1 \rightarrow 33$
$k = -1 \rightarrow 15$
$l = -24 \rightarrow 21$
3 standard reflections every 97 reflections intensity decay: negligible

Refinement

Refinement on F
$R = 0.059$
$wR = 0.069$
$S = 1.36$
5650 reflections
191 parameters
H atoms constrained
$w = 1/[\sigma^2(F) + 0.0008F^2]$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.89$ e Å^{-3}
$\Delta\rho_{\min} = -0.87$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected bond distances (Å) for (II)*

I(1)—Cu(1)	2.628 (4)	I(3)—Cu(2^{ii})	2.492 (5)
I(1)—Cu(2)	2.620 (4)	Cu(1)···Cu(2)	2.448 (7)
I(2)—Cu(1)	2.832 (4)	Cu(1)···Cu(1^{i})	2.646 (5)
I(2)—Cu(2)	2.887 (4)	Cu(2)···Cu(2^{ii})	2.691 (8)
I(2)—Cu(1^{i})	2.508 (5)	K(1)···I(1^{i})	3.589 (4)
I(3)—Cu(1)	2.714 (4)	K(1)···I(2^{i})	3.779 (5)
I(3)—Cu(2)	2.699 (4)	K(1)···I(1)	3.504 (6)

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$.

Compound (III)

Crystal data

$[Rb(C_{10}H_{20}O_5)][Cu_2I_3]$
$M_r = 813.5$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$C2/c$
$a = 24.613$ (3) Å
$b = 11.170$ (1) Å
$c = 17.211$ (3) Å
$\beta = 119.90$ (1)°
$V = 4101.9$ (9) Å^3
$Z = 8$
$D_x = 2.635$ Mg m^{-3}
D_m not measured

Cell parameters from 46 reflections
$\theta = 5.018$–12.481°
$\mu = 8.96$ mm^{-1}
$T = 301$ K
Rod
0.20 × 0.15 × 0.10 mm
Colorless

Data collection

Syntex *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Sheldrick, 1990)
$T_{\min} = 0.168$, $T_{\max} = 0.408$
6963 measured reflections
5968 independent reflections
1929 reflections with $F > 3.5\sigma(F)$

$R_{\rm int} = 0.0347$
$\theta_{\max} = 30°$
$h = -1 \rightarrow 34$
$k = -1 \rightarrow 15$
$l = -24 \rightarrow 21$
3 standard reflections every 97 reflections intensity decay: negligible

Refinement

Refinement on *F*
$R = 0.058$
$wR = 0.058$
$S = 0.93$
5968 reflections
191 parameters
H atoms constrained
$w = 1/[\sigma^2(F) + 0.0008F^2]$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.0$ e Å^{-3}
$\Delta\rho_{\min} = -0.99$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected bond distances (Å) for (III)*

I(1)—Cu(1)	2.650 (4)	I(3)—Cu(2)	2.745 (4)
I(1)—Cu(2)	2.633 (5)	I(3)—Cu(2$^{\rm ii}$)	2.529 (6)
I(2)—Cu(1)	2.872 (4)	Cu(1)···Cu(1$^{\rm i}$)	2.697 (6)
I(2)—Cu(2)	2.917 (4)	Cu(2)···Cu(2$^{\rm ii}$)	2.657 (8)
I(2)—Cu(1$^{\rm i}$)	2.538 (5)	Cu(1)···Cu(2)	2.480 (7)
I(3)—Cu(1)	2.747 (4)	Rb(1)···I(1)	3.632 (3)

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$.

Data were collected with a variable scan rate, using a $\theta/2\theta$ scan mode with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$. Refinement was completed using full-matrix least-squares methods.

For all compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXS*86; molecular graphics: *XP* (Siemens, 1990)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1047). Services for accessing these data are described at the back of the journal.

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Tetraethylammonium Dicopper(I) Triiodide and (18-Crown-6)potassium Dicopper(I) Triiodide

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Abstract

Tetraethylammonium triiododicopper(I), $(C_8H_{20}N)[Cu_2I_3]$, and (18-crown-6)potassium triiododicopper(I), $[K(C_{12}H_{24}O_6)][Cu_2I_3]$, crystallize with a polymeric series of edge-sharing Cu_2I_2 rhombs having Cu atoms bridged in pairs by an additional I atom, *i.e.* *catena*-poly-[[copper(I)-μ_2-iodo-copper(I)]-di-μ_3-iodo]. The pattern of projection of bridging μ_2-I atoms with respect to the polymeric band is up, down, up, down.

Comment

Copper(I) halide complexes have been observed to form $Cu_2I_3^-$ polymers. The polymer may be viewed as a chain of Cu_2I_2 rhombs which share opposite edges, with an additional I atom bridging the Cu atoms of every alternate rhomb. The additional bridging I atoms may show bridging on the same side of the polymeric sheet, bridging in the sequence two up, two down, *etc.*, or bridging on alternating sides of the polymer [see preceding paper (Nurtaeva & Holt, 1998)].

Two $Cu_2I_3^-$ polymers with alternating up, down, up, down projections of bridging I atoms have been reported: $[Et_4N][Cu_2I_3]$ and $[(CH_3)_2\text{—N}{=}\text{CH—N}{=}\text{CH—N}(CH_3)_2][Cu_2I_3]$ were mentioned by Hartl & Mahdjour-Hassan-Abadi (1981) without full crystallographic details (only ranges and mean values of distances were reported). In connection with a study of the emission properties of these materials, we have pre-